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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1537

*Spacecraft Adhesives for Long Life and
Extreme Environments*

W. D. Roper

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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Preface

This report summarizes the work performed by the Engineering Mechanics Division of the Jet Propulsion Laboratory for the NASA Office of Space Science Applications. The report covers the results of research efforts performed during the period July 1, 1969 to June 30, 1971.

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Abstract

A review of the state-of-the-art of high-performance adhesives was undertaken for the purpose of establishing those newer materials which show potential for future application in spacecraft. Following the state-of-the-art review, several adhesive materials were selected and evaluated in the laboratory. The adhesive materials evaluated included the polyimide, the polybenzimidazole, and the polyquinoxaline polymer systems. In the laboratory work the thermal shock resistance of each material was determined by thermal cycling through the temperature range of 204 to -73°C . In addition, each adhesive was evaluated for long-term elevated-temperature performance in aging tests conducted at 260°C and 10^{-4} N/cm² for 5000 h. The results of this investigation showed that the polyimide adhesive system currently has the greatest potential for use in future spacecraft applications.

Spacecraft Adhesives for Long Life and Extreme Environments

I. Introduction

Future planetary exploration will require spacecraft with their scientific payloads to function in environmental extremes and for mission durations that are far beyond those which have been attempted thus far. The Outer Planet Grand Tour missions are typical of these future missions. In these flights, extreme cold [-225°C (-375°F)]¹ for periods extending up to 12 yr is anticipated. Although portions of the spacecraft will be thermally controlled for satisfactory operation of electronics and propulsion subsystems, some external components (antenna, instrument booms, etc.) may be subjected to the full temperature extreme.

At the other end of the temperature scale, near-sun missions (Venus, Mercury, solar probes) will require the spacecraft to function in high-temperature environments. Components such as sun sensors, thermal shields, and solar panels will be required to function for extended periods at temperatures in excess of 204°C (400°F). It is also anticipated that large and rapid thermal transients

will also be encountered, particularly during periods of sun occultation and maneuvers of the spacecraft.

These new environments will impose extremely high demands on spacecraft materials. This is particularly true of the adhesive materials which are widely used within the spacecraft in both structural and nonstructural applications. An extremely long life and high reliability will be demanded of these materials in the new environmental extremes.

In order to accomplish the future planetary missions, some effort must therefore be made to select those adhesive systems that can meet the rigorous performance expected. This was the intent of this investigation. To accomplish this objective, a two-phase approach was undertaken. In the first phase, a general review of the literature was made in order to establish which new polymer systems had potential as adhesives. The review was to include not only the published literature, but contact with many of the commercial producers of adhesive materials. In the second phase of the work, selected adhesive materials would then undergo some limited laboratory testing in order to characterize them as potential spacecraft adhesives. The selected materials would

¹Values in customary units are included in parentheses after values in SI (International System) units if the customary units were used in the measurements or calculations.

be tested for their adhesive strength in both high- and low-temperature environments and also under conditions of severe thermal shock. The test conditions would be simulations of those to be encountered in future planetary missions. It was anticipated that the information obtained in this investigation would be valuable in the design of future spacecraft. This report describes the results of Phase 1 and the elevated-temperature portion of Phase 2, as well as limited thermal shock tests. The low-temperature portion of Phase 2 is not included in this report.

II. Adhesive Materials Review

A high-performance adhesive, as defined in this study, is one which exhibits long-term (1000 h or more) performance at temperatures in excess of 204°C (400°F) and in the cryogenic region of -196°C (-320°F) and lower. The ability of the adhesive to exhibit such a performance will depend to a large extent on the intrinsic properties of the basic polymer that comprise the major portion of the adhesive. In some cases the minor constituents—stabilizers, plasticizers, etc.—may also be important in producing the high performance of a particular adhesive system. However, for achieving performance in the more severe space environments anticipated, the use of these minor additives becomes more and more restrictive, and ultimately their use is completely precluded. The basic characteristics of the primary polymeric material is therefore of fundamental importance.

A review of some of the general features of the more recent polymer systems is therefore of interest in determining future high-performance spacecraft adhesives. This review provides an understanding of some of the approaches that researchers have been following in order to form polymers with greater stability in severe environmental extremes. Table 1 lists some of the newer systems that have been researched during the last decade. Some of these have achieved commercial availability while others have been dropped or are under continuing research. The polymer systems shown in Table 1 can be roughly classed, according to structure, as either simple linear, semiladder or ladder polymers. The simple linear polymers refer to those whose polymeric chain primarily consists of carbon-to-carbon bonds that form an essentially linear structure. This structure permits considerable freedom for segmental rotation of the polymer chain. The polymers of this type may be rigidified by adding appropriate pendant groups along the chain or by chemical cross-linking of the chains.

Recently, a new generation of polymers (the so-called ladder and semiladder polymers) has been researched. These polymers possess inherently rigid chains and are formed by the linking of aromatic or heterocyclic rings. Figure 1 illustrates the general nature of these polymer structures. Although the polymers are essentially linear, some cross-linking does occur in a few incidences.

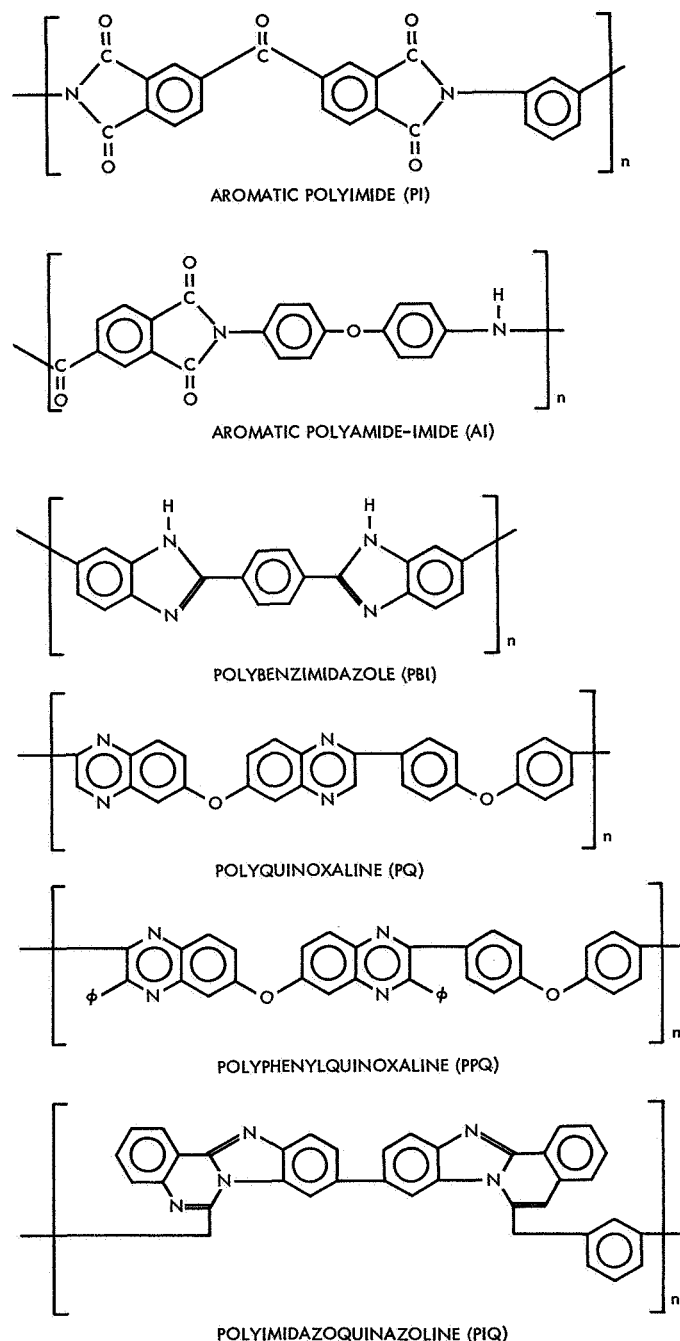


Fig. 1. Typical (idealized) structure of high-performance adhesive materials

Table 1. Typical thermal properties of some recently researched polymeric materials

Polymer systems	Structural class	Glass transition temperature (T_g), °C	Polymer softening/melting temperature (approx), °C	TGA data, ^a °C	References
Aromatic polysulphone	Simple linear	—100, 190	349–400	500–550	(1)
Aromatic polyamide-imide (AI)	Semiladder	266	400	400 ^b	(2)
Polybenzimidazole (PBI)	Semiladder	—70, 310, 430	Decomposes	250	(2,3)
Polybenzothiazole (PBS)	Semiladder	288	Decomposes	600	(4)
Polybenzoxazole (PBO)	Semiladder	413–435	Decomposes	400–600	(5)
Aromatic polyimide (PI)	Semiladder	266–380	Decomposes	377–419	(2,6)
Polyquinoxaline (PQ)	Semiladder	382–390	Decomposes	500	(7)
Polyphenylquinoxaline (PPQ)	Semiladder	402–432	Decomposes	550	(7)
Polyimidazoquinazoline (PIQ)	Semiladder	—	Decomposes	316 ^c	(8)
Polyiminobenzoxazole	Semiladder	—	175–225	400 ^b	(9)
Polyiminobenzothiazole	Semiladder	—	149–199	300 ^b	(9)
Polyimidazopyrrolone (PIP, Pyrrene)	Ladder	473	Decomposes	400–500	(2,10)
Polyimidazobenzophenanthroline (BBB and BBL)	Ladder	—	Decomposes	400–450	(11)
Carboranylene siloxane	Simple linear	—34	205	—	(12,13)
Diazadiphosphetidine	Ladder	—	Decomposes	350–475	(14)

^aTypical thermogravimetric analysis (TGA) data for representative polymers. Temperatures shown indicate onset of polymer decomposition in air.

^bTGA data taken in nitrogen.

^cTemperature for an isothermal weight loss of 4% after 120 h in air.

Research emphasis has recently been focused on these semiladder and ladder polymers. These have been prime candidates for high-temperature applications as adhesives, laminating resins, films, etc. For high-temperature applications, researchers have been attempting to achieve higher glass transition temperatures (T_g). At the polymer T_g , softening and other property changes abruptly occur (e.g., specific volume), which then detract from the useful mechanical properties of the polymer. Consequently, the higher the T_g , the higher will be the polymer use temperature.

One approach to achieve high T_g materials has been the reduction or complete elimination of divalent atoms, such as oxygen, within the polymer chain. Atoms of this type tend to lower the T_g values as they provide considerable rotation to the polymer chain. A second approach to high T_g materials has been the research of the heterocyclic ring structures (ladder and semiladder polymers). These materials not only possess high T_g 's but also much higher melting points due to polymer chain rigidity and lack of rotational freedom within the polymer structure.

Table 1 clearly shows the extent to which the search for the high T_g materials has been achieved. Glass transition temperatures ranging from approximately 260 to 480°C are typical of these new semiladder and ladder polymers. Many of the materials exhibit no discrete melting or softening point and tend to decompose on heating, leaving only solid residues.

The aromatic and heterocyclic polymers have also been extensively researched for their potential for thermal stability. The aromatic and heterocyclic rings contribute to high-resonance bond energies and, consequently, high resistance to thermal decomposition. The primary method for evaluating and comparing the stabilities of various materials is by thermogravimetric analysis (TGA). In this technique, a sample is heated at a constant rate on a thermobalance in air, an inert atmosphere, or in a vacuum, and the sample's weight change versus temperature is recorded. Under the conditions of the test, initiation of the material's decomposition is indicated by a sudden reduction in the sample's weight. Table 1 shows typical TGA data that have been reported for the newer polymeric materials. The ranges shown for some

of the listed polymers result from data obtained for different analogues of the same basic polymer structure. In general, these data show that the new polymers have thermal stabilities that are quite high.

In the area of the inorganic or semiorganic polymers, some development efforts are being made. Investigation of these materials has been prompted by the high thermal stability that has been achieved in the past with the silicon polymers. Bond energy considerations indicate that greater thermal stability can be ultimately achieved with inorganic polymers (which involve ionic bonding) compared with organic polymers (involving covalent bonding). Table 1 shows two typical semiorganic polymers—the carboranylenesiloxanes and diazadiphosphetidines. The former is a boron-silicon linear polymer (Refs. 12 and 13), which is commercially available as an elastomeric material (Dexsil), and the latter is a developmental material, which is a complex organophosphorous resin (Ref. 14).

In addition, other promising new semiorganic polymers—the so-called “coordination polymers”—are being researched as potential high-temperature polymers. In these studies attempts are being made to form polymers from such metals as chromium, beryllium, copper, and nickel (Refs. 15, 16, and 17). In these polymers certain atoms, such as nitrogen and oxygen, donate electrons to the metals to form coordinate bonds. The polymers generally exhibit chain rigidity due to incorporation of ring structures. Low solubility, poor flexibility, and low molecular weight are some of the problems to be solved with these materials.

In general, the new semiorganics cannot be considered immediately for spacecraft adhesive use as considerably more development is required. However, in the future they may prove to be excellent candidates for spacecraft adhesives.

For performance as adhesives in cryogenic environments, the room temperature vulcanizing (RTV) silicones and the polyurethanes have been widely used materials. The methyl and phenyl RTV silicones have been evaluated at temperatures as low as -253°C (-423°F) (Ref. 18); however, their normal long-term operating range has been limited to -107 to 204°C (-160 to $+400^{\circ}\text{F}$) where elastomeric properties are required. Adhesive lap shear strength is reported to be unchanged between room temperature and -253°C . At room temperature, test specimen failures are cohesive, whereas at -253°C the failures are adhesive. Embrittlement of the

Table 2. High-performance adhesive materials

Polymer type	Trade name	Manufacturer/developer
Polyimide	FM-34	American Cyanamid Co. Bloomington Dept. Havre de Grace, Md.
	Metlbond 840	Whittaker Corp. Narmco Materials Div. Costa Mesa, Calif.
	PI-5505	E.I. duPont de Nemours & Co. Fabrics & Finishes Dept. Philadelphia, Pa.
Polyamide-imide	AI-1030 AI-1137	Amoco Chemicals Corp. Chicago, Ill.
Polybenzimidazole	Imidite 850	Whittaker Corp. Narmco Materials Div. Costa Mesa, Calif.
Polyquinoxaline	PQ (Developmental)	Whittaker Corp. Narmco R & D Div. San Diego, Calif.
Polyphenylquinoxaline	PPQ (Developmental)	Whittaker Corp. Narmco R & D Div. San Diego, Calif.
Polyimidazoquinazoline	PIQ (Developmental)	Whittaker Corp. Narmco R & D Div. San Diego, Calif.

materials is therefore evidenced at cryogenic temperatures. These materials can only be considered in non-structural adhesive applications due to their limited adhesive strength in lap shear which approximates 3.5 MN/m^2 (500 psi).

Many polyurethane-based adhesives are commercially available and have been widely used in cryogenic environments. Adhesive lap shear strengths in the structural adhesive range [approximately 35 – 55 MN/m^2 (5000–8000 psi)] with accompanying high peel strengths have been reported at temperatures as low as -253°C (Ref. 19). However, these materials are limited to a maximum elevated use temperature of approximately $+120^{\circ}\text{C}$ (248°F).

It has been found that many of the recent aromatic heterocyclic polymers, which have been developed primarily for elevated-temperature use, also show good cryogenic performance in composites and adhesives. It is believed that a combination of linearity, high density, and high glass transition temperature (T_g), which are consequences of aromatic-heterocyclic structure, makes possible a stress release mechanism in these materials at low temperatures (Ref. 20).

All of the polymers listed in Table 1 do not show potential as adhesive materials. Many can only be considered as laminating resins (e.g., in composites) since they are too rigid, when cured, to be useful as adhesives. Table 2 lists the polymers that may be currently considered as potential spacecraft adhesive materials. Typical chemical structures of these materials are shown in Fig. 1. Some of these materials are commercially available, whereas some are at present only developmental materials. It is interesting to note that the listed adhesives are all of the aromatic-heterocyclic polymer class. As discussed earlier, this type of polymer presently shows the best promise as a high-temperature material. No new semiorganic polymer, which exceeds the performance of the current silicones, is presently available for consideration as an adhesive material.

The polymer types which have already established commercial availability as adhesives are the polyimide (PI), the polyamide-imide (AI), and the polybenzimidazole (PBI). Figures 2 and 3 show reported adhesive lap shear data on these commercial materials. The figures show some comparison between these adhesives on the basis of their long- and short-term elevated-temperature performance (in air). In the bonding of stainless steel, PBI is shown (Fig. 2) to have better short-term thermal stability than PI. Comparable data on titanium could not be found during the adhesive review. However, some

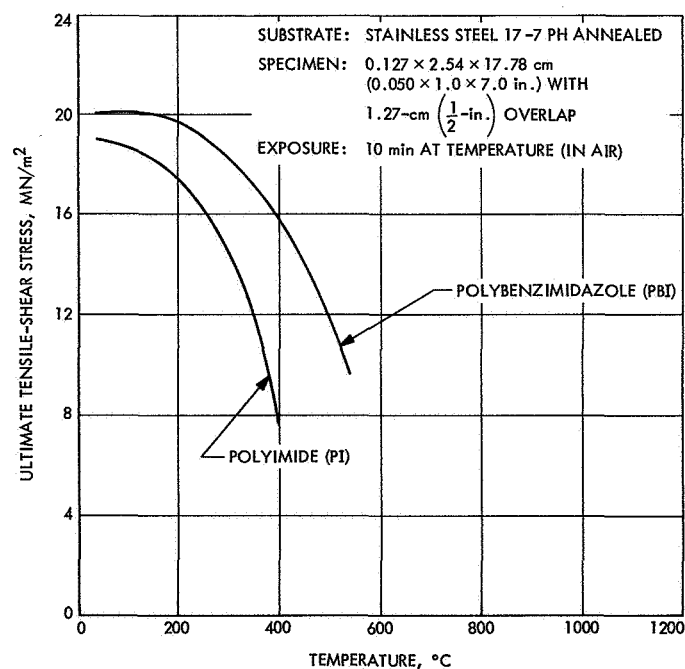


Fig. 2. Comparison of elevated-temperature performance of polyimide and polybenzimidazole (Refs. 21 and 22)

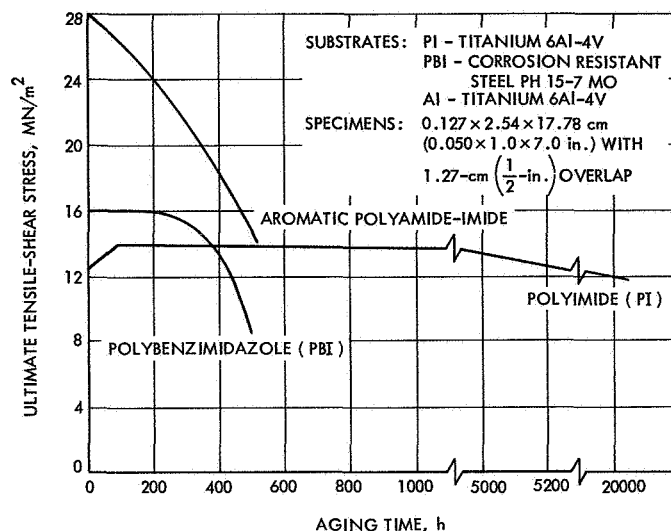


Fig. 3. Comparison of long-term aging in air at 260°C (500°F) of high-performance adhesives (Refs. 21, 23, and 24)

titanium data (Fig. 3) shows PI to have an excellent long-term performance at 260°C (500°F). The main feature of the AI adhesive is its high initial strength; however, it is shown to be inferior to PI from the standpoint of aging at the elevated temperature. The commercial PI and PBI materials are commonly supplied as film adhesives with fiberglass carriers. At present, the AI material is sold as a liquid resin which must be further processed by the user into an adhesive. Aluminum powder can be compounded into the AI resin in order to improve its thermal performance. The aluminum-filled AI resin can then be processed into a glass-supported film adhesive or it may be used directly as a paste-type adhesive.

One of the major problems with all of these commercial materials is the fact that their polymerization or cures involve condensation-type reactions. This results in the evolution of volatile reaction products (i.e., water, phenol) during cure which, if not properly controlled, will result in bonds with high porosity. Perforated substrates are sometimes required to facilitate removal of volatiles during cure. Research is presently being undertaken to reduce the amount of volatiles produced with the polyimide system. One improved PI system has already been commercially developed (Ref. 6), but at present it is restricted for use only in composites. Development of this improved PI into an adhesive material is presently being pursued.²

²Personal communication from R. Sproul, TRW Systems Group, Redondo Beach, Calif.

Of the three commercial materials, PBI has the most rigorous and extensive curing system. Curing pressures between 0.1 and 1.4 MN/m² (15 and 200 psi) are used with PBI as well as stepwise curing from 221 to 316°C (430 to 600°F). In some cases, a 400°C (750°F) post-cure in a nitrogen atmosphere is required for optimum bond strength. These elevated curing temperatures significantly limit the use of PBI in bonding applications. The PI curing system is not as rigorous. Curing pressures of the order of 0.15 MN/m² (25 psi) and a curing temperature of 177°C (350°F) with a 288°C (550°F) post-cure are usual with the PI materials. The AI system requires a 288°C (550°F) cure with a 316°C (600°F) post-cure.

The chemical structure of the developmental materials PQ, PPQ, and PIQ are shown in Fig. 1. These materials are also formed by condensation-type polymerizations. Therefore, evolution of volatiles during cure also occurs with these materials. High curing temperatures, 316–400°C (600–750°F), and pressures are also anticipated with these materials.

Although PQ is still considered as a developmental material, it can be commercially obtained as a resin solution. In order for this material to achieve commercial importance as an adhesive, its thermal performance will have to exceed that of the current PI materials. This would mean that its continuous-use temperature would have to exceed approximately 260°C (500°F). At the time of this review, long-term elevated-temperature aging data was not available on PQ, but it was believed that PQ should exceed 316°C (600°F) (Ref. 15). Also, no data have been published on its cryogenic performance as an adhesive. As with most materials with high T_g values, the cryogenic performance of PQ should be quite good.

The other developmental materials, PIQ and PPQ, show the most promise of exceeding the performance of PQ. It has been reported that PIQ performs at 538°C (1000°F) for 10 min and that efforts are being made to extend that to about 1 h (Ref. 15). At present, no cryogenic performance data on these materials as adhesives have been reported. Only PPQ is currently available commercially on a restricted basis. It is reported that PIQ, which is still under extensive development, will not be commercially available, if at all, for some time in the future.³

³Personal communication from W. P. Fitzgerald, Whittaker Corp., R&D Division, San Diego, Calif.

III. Experimental Section

A. Spacecraft Adhesives Selection and Testing

Following the Phase 1 adhesives review, a selection of the new materials with the greatest potential for future spacecraft use was made. The selected candidates were then tested in the laboratory in order to establish more fully their suitability for use in spacecraft applications. One of the criteria used in the selection was that each new material should be presently available commercially. Because of this, both the PPQ and PIQ materials could not be considered for testing as they still required considerably more development and were not readily available. The amide-imide system did not appear to have any distinct advantage over the polyimides as their long-term performance at elevated temperatures was reported to be below that of the polyimides. Consequently, those with the most immediate promise for spacecraft use were the polyimide, the polybenzimidazole, and the polyquinoxaline materials.

The commercial polyimide that was selected for testing was the FM-34 adhesive (American Cyanamid Co., Bloomingdale Dept.), and the selected polybenzimidazole was Imidite 850 (Whittaker Corp., Narmco Materials Division). Both of these adhesives were supplied as films supported by fiberglass carriers. The polyquinoxaline material was purchased as a liquid resin (PQ resin, Whittaker Corp., Research and Development Division). This material required further processing in order to prepare it as a glass-supported adhesive film. For comparison purposes a typical epoxy paste-type adhesive, EA913 (Hysol Corp.), was also selected for testing along with the newer materials. This particular epoxy adhesive was selected because it had been used in the past in spacecraft applications. It, therefore, would provide a comparison in the laboratory testing of the newer adhesive materials.

An outline of the laboratory testing that was performed on the adhesives is shown in Fig. 4. Following the adhesive selection, two exposures were performed on each material: a thermal shock test, and long-term vacuum-thermal exposure. This testing was designed to evaluate the metal-to-metal bonding of the adhesives in simulated spacecraft environments. Each adhesive evaluated was prepared in standard lap shear specimens according to the ASTM D1002 (American Society for Testing and Materials) test procedure. The effect of the various exposures on each adhesive was determined by tensile testing of the lap shear specimens following the exposures using the ASTM D1002 test method.

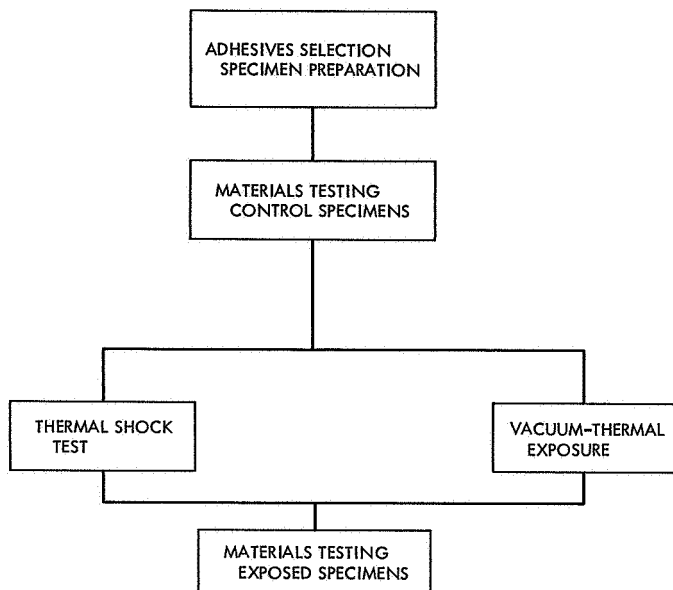


Fig. 4. Laboratory testing sequence

Since the cure temperatures and service temperatures of the tested adhesives were well above 260°C (500°F), only high-temperature substrates could be used. Consequently, the adhesives in these studies were evaluated for their metal-to-metal bonding of titanium. The lap shear specimens were, therefore, prepared using titanium adherends (6Al-4V alloy). This particular substrate would be the material most likely used with the high-temperature adhesives in any future spacecraft design. In the case of the epoxy adhesive, which was used for comparison purposes, a typical spacecraft aluminum alloy (6061) was used. All tested adhesives except the polyquinoxaline were received in a fully formulated adhesive form. The polyquinoxaline required special formulation and processing in order to prepare lap shear specimens from it. The procedures followed for the preparation of all the lap shear specimens are given in detail in the appendix of this report.

B. Thermal Shock Testing of Adhesives

The evaluation of the thermal shock resistance of a candidate spacecraft adhesive is very necessary for its ultimate acceptance as a spacecraft material. The thermal shock test performed in these studies was designed to simulate a condition typical of what might be expected in a near-sun mission (Mercury or Venus flyby). In this case, rapid structural temperature changes between 204 and -73°C (400 and -100°F) temperature extremes were used. Some *in situ* adhesion testing of the candidates was also performed at the -74°C (-100°F) extreme as well as testing before and after the cycling. As

seen from Fig. 5, the thermal shock rates experienced by the adhesives ranged from 14 to 30°C/min (25 to 55°F/min). A thermal shock of this order could be considered typical of a Venus-type mission (Ref. 25).

The procedure used in the thermal shock testing of the adhesives was as follows:

- (1) Lap shear test specimens of each adhesive were tested at room temperature in order to establish their room-temperature strength. The specimens were tested according to the ASTM D1002 test method.
- (2) Specimens of each adhesive were then placed in a preheated $204 \pm 5^\circ\text{C}$ ($400 \pm 10^\circ\text{F}$) oven. The warm-up of the specimens was monitored by a temperature recorder using thermocouples mounted on the specimens.
- (3) When the specimens reached $204 \pm 5^\circ\text{C}$, they were allowed to soak at that temperature for 10-15 min. They were then removed and quickly placed inside a prechilled $-73 \pm 5^\circ\text{C}$ ($-100 \pm 10^\circ\text{F}$) chamber. The specimen cool-down was again continuously recorded during the cooling process.
- (4) After the specimens reached $-73 \pm 5^\circ\text{C}$, specimens of each adhesive were pulled *in situ* according to the ASTM D1002 test method.
- (5) Following the -73°C testing, the remaining specimens were again rapidly heated to $204 \pm 5^\circ\text{C}$ in the preheated oven.
- (6) After soaking at $204 \pm 5^\circ\text{C}$ for 10-15 min, the specimens were then removed from the oven and again rapidly chilled in the $-73 \pm 5^\circ\text{C}$ chamber. Specimens of each adhesive were then tested *in situ* at the -73°C temperature.

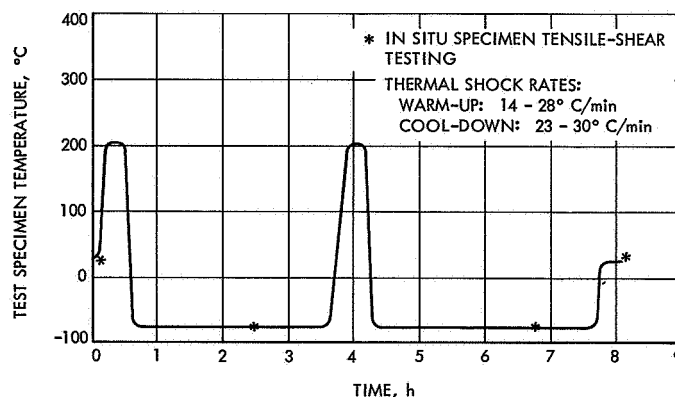


Fig. 5. Adhesive thermal shock test data

- (7) Following the second chilling and *in situ* testing, the last remaining specimens were then warmed to room temperature and tested at this temperature.

In addition to the preceding specimen testing, an attempt was also made to evaluate the creep resistance of the FM-34 and the PQ adhesives. To accomplish this, one creep test specimen of each adhesive was prepared according to the ASTM D2294 test procedure. Each specimen was mounted in a creep test fixture using a 5.4-MN/m² (750 psi) tensile load. The specimens were then subjected to the same thermal shock test as performed on the lap shear specimens. The specimens were monitored for evidence of creep or bond failure during this thermal shock exposure. Replicate specimens were not run due to limitations in test fixtures.

C. Long-Term Vacuum-Thermal Exposure of Adhesives

In order to further qualify the candidate adhesives for spacecraft use, some evaluation of their aging properties at high temperatures was necessary. In these studies the candidate adhesives were given a long-term exposure at 260°C (500°F) in a vacuum environment of 10⁻⁴ N/cm² (10⁻⁶ torr). This exposure was selected to simulate a non-thermally controlled spacecraft environment during a near-sun mission such as that to Venus or Mercury. The procedure followed in this testing is outlined in the following discussion.

Lap shear specimens of each adhesive were soaked at 260 ± 5°C for approximately 10–15 min. The specimens were then tested at this temperature to determine their lap shear adhesive strength. Three to four additional specimens of each adhesive were then placed in a pre-heated vacuum-thermal chamber and the specimens were heated to 260 ± 5°C in a vacuum of 10⁻⁴ N/cm² for a continuous period of 5054 h. At the end of this time, the specimens were pulled at 260 ± 5°C (atmosphere pressure) in a tensile machine according to ASTM D1002. The lap shear adhesive strength of each adhesive was thus evaluated both before and after the high-temperature vacuum-thermal exposure.

IV. Results and Discussion

A. Thermal Shock Testing of Adhesives

The lap shear adhesion data obtained on each adhesive during the thermal shock testing are shown in Table 3. The data include lap shear strength of the adhesives at room temperature prior to cycling, at -73°C (-100°F)

Table 3. Thermal shock test data

Adhesive material	Tensile—shear strength, MN/m ²				Adhesive creep, ^b mm	
	Cycle 1 ^a		Cycle 2 ^a			
	24°C	−73°C	−73°C	24°C		
Imidite 850 (PBI)	11.4 9.5 10.1 10.8	8.1 7.9 9.6	7.3 8.7	7.7 7.7 9.5	Not tested	
Av	10.4	8.1	8.0	8.3		
FM-34 (PI)	18.0 11.3 19.0	19.0 17.0 19.0	15.0 18.0 22.0	13.0 11.3 ^c 9.9 ^c		None
Av	16.0	18.5	18.5			
Polyquinoxaline (PQ)	11.8 15.0 8.9	13.2 10.0	8.5 10.7	12.6 16.0	None	
Av	11.8	11.6	9.6	14.5		
EA 913 (Epoxy)	21.0 29.0 30.0	12.1 14.0 12.8	10.8 13.5	27.0 26.5 26.0		Not tested
Av	27.0	13.1	12.2	26.5		

^aSee Fig. 5.

^bSee Section III-B.

^cDefective specimen.

^aSee Fig. 5.

^bSee Section III-8.

^cDefective specimen.

during cycling, and again at room temperature at the end of the two thermal cycles. These data permit some evaluation of the overall effect of the cycling as well as some evaluation of the adhesives at the lower-temperature extreme. Resources did not permit testing at the 204°C (400°F) temperature extreme. Table 3 also shows the results obtained with the creep test specimens that were also subjected to the same thermal cycling.

Of all the newer adhesives tested, the polyimide (FM-34) gave the highest bond strength at room temperature. The polyquinoxaline was only slightly higher in strength than the polybenzimidazole (Imidite 850). The epoxy adhesive (EA913) had the greatest strength of all. However, it should be noted that the epoxy bonding was on aluminum, whereas the new high-temperature adhesives were on titanium. Bond strengths are generally lower on titanium substrates as compared to aluminum or steel alloys.

The data obtained on the polybenzimidazole adhesive (Imidite 850) was particularly interesting. The two ther-

mal cycles resulted in an overall bond strength loss of approximately 20%. The data indicate that this loss occurred during the first cycle. After the first cycle the bond strength remained essentially constant at the 20% lower level. Statistical treatment of the data indicated that this strength loss was real to a better than 95% confidence level. The strength loss after the first cycle was apparently nonrecoverable upon rewarming to room temperature. No difference in the mode of specimen failure was observed during the pulling of the specimens. The specimen failure was in all instances 90% or more cohesive (failure within the adhesive).

The cause of the strength loss was not determined, because of the limited scope of this program. It is suspected that bond damage occurred during the chilling phase of the first cycle due to thermal contraction effects. As noted earlier, in the adhesives review, some polybenzimidazoles may exhibit more than one glass transition temperature. One PBI polymer has been found to have three, one of which is in the region of -70°C (-94°F) (Ref. 3). The PBI adhesive evaluated in these studies may also exhibit some low T_g value. If this is the case, it may account for the apparent loss in bond strength that occurred upon chilling the adhesive to -73°C (-100°F). If the material had passed through a low-temperature T_g , then some bond damage may have occurred due to resultant physical property changes of the adhesive. Another cause may have simply been that the PBI structure was too rigid to adequately respond to the rapid thermal shock imposed.

The data obtained on the polyimide adhesive (FM-34) showed that the adhesive tensile-shear strength at room temperature and -73°C (-100°F) was essentially the same. No significant embrittlement of the adhesive occurred at the low temperature. The mode of specimen failure with all the specimens was 90% or more cohesive. No creep was exhibited by the creep test specimens which were also thermal-cycled with a 5.3-MN/m^2 (750 psi) tensile load. Investigation of the two low tensile-shear values 11.3 and 9.9 MN/m^2 (1610 and 1420 psi) in the final room-temperature tests revealed that these specimens were defective due to panel misalignment during bonding. These values were not, therefore, averaged as they were not representative of good specimens. Since all the other specimens tested throughout the cycling showed essentially the same strength, it was apparent that the thermal cycling had not affected the adhesive. This observation was also in line with the fact that all reported T_g values for polyimides are in excess of 260°C (500°F). Therefore, it did not seem likely that the chill-

ing of the polyimide adhesive to -73°C (-100°F) should affect the adhesive performance due to passage through a T_g region.

The polyquinoxaline adhesive also did not seem affected by the thermal shock cycling. Its low-temperature strength was essentially the same as that at room temperature. No creep was obtained with the creep test specimens which were thermal-cycled with a 5.3-MN/m^2 tensile load. The specimen failures during testing were approximately 40% cohesive. This indicated that the bond strength obtained was not optimized. Inexperience in the processing and formulation of the resin into an adhesive material was very likely a cause. No attempt was made to optimize the processing of this material into high-strength bonds. It was conceivable that higher bond strengths can be achieved with further development of this material as an adhesive.

The epoxy adhesive, EA913, was given the thermal shock cycling to compare its performance with that of the newer adhesive materials. As can be seen from the test data, the adhesive has high room-temperature strength which drops considerably at -73°C (-100°F). This is not too surprising as epoxy adhesives are generally reported to have brittle points in the region of -57°C (-70°F). The mode of failure for the specimens pulled at room temperature was almost 100% cohesive. The mode was significantly different at -73°C . At this low temperature, the specimens pulled only 30–40% cohesively. Adhesive strength loss at the low temperature was very evident. However, the loss was reversible as the adhesive regained its room-temperature strength after the cycling. At room temperature, after the two thermal cycles, the specimens also pulled about 100% cohesively. The thermal cycling, therefore, did not apparently damage the adhesive.

B. Long-Term Vacuum-Thermal Exposure of Adhesives

The test data obtained from the long-term vacuum-thermal exposure are given in Table 4. These data show lap shear strengths of the various adhesives at 260°C (500°F) both before and after a 5054-h exposure at 260°C and 10^{-4}-N/cm^2 pressure.

The long-term exposure did not apparently change the strength of the polyimide. However, a comparison with room-temperature data (Table 3) showed that the PI lost approximately 30% of its strength in going from room temperature (24°C) to 260°C . The specimen failure modes at 260°C were the same as that at room tempera-

Table 4. Long-term vacuum-thermal exposure test data

Adhesive	Tensile-shear strength at 260°C, MN/m ²	
	Control	Exposed
Imidite 850 (PBI)	7.5	9.8
	8.1	8.3
	7.1	9.1
	Av 7.6	9.0
FM-34 (PI)	11.1	10.1
	11.6	12.0
		9.7
		13.7
	Av 11.4	11.4
Polyquinoxaline (PQ)	6.8	8.1
	6.6	7.7
	6.3	10.0
	6.2	9.6
	Av 6.5	8.9
Specimen exposure: 260°C (500°F) at 10 ⁻⁴ N/cm ² (10 ⁻⁶ torr) for 5054 h		
Specimen testing: According to ASTM D-1002 after 10-min soak at 260°C (500°F)		

ture—90% or more cohesive. The modes before and after the long-term exposure were the same.

The polyquinoxaline adhesive showed a 25% increase in strength after the exposure. This was probably due to additional cure given to the adhesive during the exposure. However, its initial strength at 260°C was appreciably lower than that at 24°C (Table 3). The specimen mode of failure was in all instances approximately 40% cohesive.

The polybenzimidazole adhesive also showed an increase in strength after the exposure period. This amounted to approximately 15%. The 260°C strength was also approximately 25% below that at room temperature (24°C). The mode of specimen failure at 260°C was 90% or more cohesive which was identical to that obtained at room temperature.

Figure 6 graphically shows the comparison in performance that was exhibited by each of the tested adhesives. The polyimide adhesive (FM-34) exhibited the highest bond strength of all tested adhesives both before and after the exposure. Prior to exposure the polybenzimidazole (PBI) adhesive was only slightly higher than the polyquinoxaline (PQ) at 260°C. These data showed

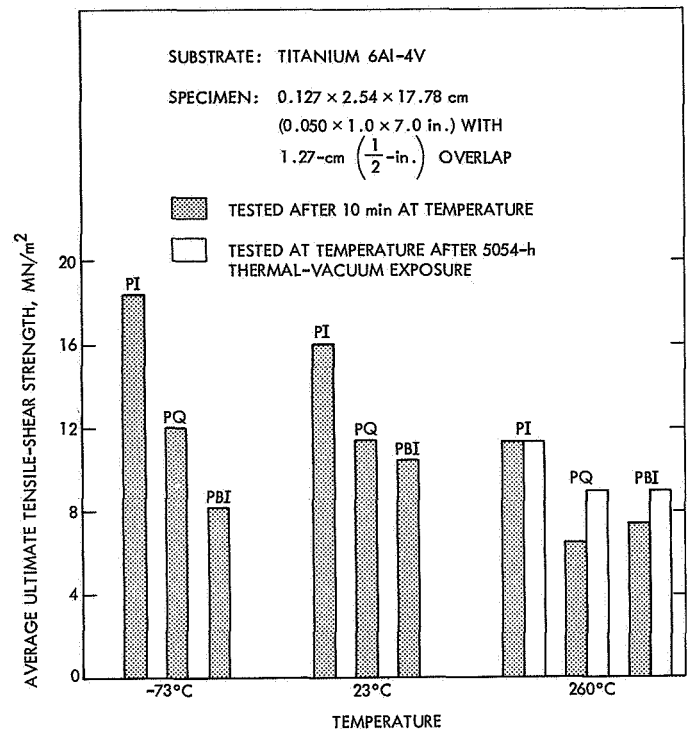


Fig. 6. Adhesive strength test data

very clearly the superiority in performance that was exhibited by the polyimide system. The polyimide adhesive, therefore, showed excellent potential for use in future spacecraft.

V. Conclusions

The work accomplished thus far in this investigation has shown the polyimide adhesive system to be an excellent candidate for future spacecraft applications. This is particularly true for elevated-temperature performance. In this regard the polyimide should find possible use in future near-sun missions.

The investigation has also shown that the polyquinoxaline and the polybenzimidazole systems offer no advantage over the polyimide when used to bond titanium adherends. Aside from their lower adhesive strength on titanium, they are also considerably more difficult to process into adhesive bonds.

The polyimide adhesive requires further evaluation at cryogenic temperature levels in order to determine its potential for use in future outer-planet missions. Work in this area, on both the polyimide and other candidate low-temperature materials, is in progress.

Appendix

Test Specimen Preparation

I. Surface Preparation of Lap Shear Test Panels

A. Titanium Panels

The 1.3-mm (0.050-in.) titanium (6Al-4V) panels, from which the lap shear test specimens were prepared, were fabricated according to the "Optional Panel" design of the ASTM D1002 test method. The cleaning and preparation of these panels was accomplished as follows. The panels were:

- (1) Solvent-wiped with cellulose tissues dampened with methylethyl ketone (MEK) solvent.
 - (2) Immersed in an Altrex alkaline cleaner at 70–80°C (160–180°F) for 8–12 min.
 - (3) Rinsed with hot 50–60°C (120–140°F) tap water, then cold tap water.
 - (4) Pickled in the following water solution at room temperature for 5 min:
Nitric acid—15% by weight
Hydrofluoric acid—3% by weight
 - (5) Rinsed in tap water at room temperature.
 - (6) Dipped into Pasa Jell 107 liquid (Products Research & Chemical Corp., SEMCO Division).
 - (7) Allowed to dry for 20 min.
 - (8) Rinsed thoroughly with water.
 - (9) Air- or oven-dried at less than 66°C (150°F) for 1 h.
 - (10) Stored in a clean environment. Bonding or priming of the panels was done within 2 h.
- (4) Immersed for 10–12 min in a solution of the following composition at 66 to 70°C (150 to 160°F):
Demineralized water 0.38 m³ (100 gal)
Sulfuric acid (66° Baume, technical) 126 kg (280 lb)
Sodium dichromate (dihydrate, technical) 12.6 kg (28 lb)
 - (5) Rinsed in room-temperature tap water.
 - (6) Rinsed in demineralized water.
 - (7) Air- or oven-dried at less than 66°C (150°F) for a maximum of 1 h.
 - (8) Stored in a clean environment. Bonding of the panels was performed within 2 h.

B. Aluminum Panels

Aluminum lap shear panels, 1.6 mm (0.062 in., 6061-T6), were machined according to the "Standard Panel" design of ASTM D1002. The panels were:

- (1) Solvent-wiped with cellulose tissues dampened with MEK solvent.
- (2) Immersed in an Altrex alkaline cleaner at 70 to 80°C (160 to 180°F) for 8–12 min.
- (3) Rinsed with hot 50–60°C (120–140°F) tap water.

II. Test Specimen Preparation—FM-34 Adhesive

A. Specimen Description

The FM-34 adhesive was supplied as a fiberglass-supported film adhesive. Standard lap shear test specimens (ASTM D1002) were prepared from this adhesive using 1.3-mm (0.050-in.) titanium (6Al-4V) panels. The panels were cleaned as outlined in *Section I* of this appendix.

B. Primer Application

BR-34 primer, as supplied by the FM-34 adhesive manufacturer, was brush-coated onto the bonding surfaces of the titanium panels. The dried primer thickness was held to 0.03 mm (1 mil) to 0.05 mm (2 mils). After brush-coating the titanium panels, the primer was air-dried for 30 min at room temperature, oven-dried for 30 min at 104 ± 2°C (220 ± 5°F), and finally dried for 45 min at 210 ± 2°C (410 ± 5°F).

C. Panel Bonding

A standard (ASTM D1002) panel layup was prepared from the primed titanium panels and FM-34 adhesive. The panel assembly was given the following stepwise cures using a heated platen hydraulic press:

30-min warm-up up to 288 ± 2°C (550 ± 5°F)

90-min cure at $288 \pm 2^\circ\text{C}$ ($550 \pm 5^\circ\text{F}$) and 0.3-MN/m^2 (40-psi) bonding pressure

The cured bonded panels were then given the following post-cure:

The panels were placed in a preheated oven at $177 \pm 2^\circ\text{C}$ ($350 \pm 5^\circ\text{F}$). The temperature was then raised to $288 \pm 2^\circ\text{C}$ ($550 \pm 5^\circ\text{F}$) in approximately 60 min and then held 2 h at this temperature.

III. Test Specimen Preparation—Imidite 850 Adhesive

A. Specimen Description

The Imidite 850 adhesive was supplied as a fiberglass-supported film adhesive. Standard lap shear test specimens (ASTM D1002) were prepared from this adhesive using 1.3-mm (0.050-in.) titanium (6Al-4V) panels. The panels were cleaned as outlined in *Section I* of this appendix.

B. Primer Application

Imidite 2321 primer was prepared as a solution in pyridine according to the manufacturer's recommended procedure (Whittaker Corp., Narmco Materials Division). A 0.03-mm (1-mil) coat of the primer solution was applied by brushing to the bonding surfaces of the titanium panels. The primer was air-dried 30 min at room temperature and then forced-air-dried in an air-circulating oven for 60–90 min at $93 \pm 2^\circ\text{C}$ ($200 \pm 5^\circ\text{F}$).

C. Panel Bonding

A standard (ASTM D1002) panel layup was prepared from the primed titanium panels and the Imidite 850 adhesive. The panels were cured in a heated platen hydraulic press using the following cure schedule:

Cure	Step 1	Step 2	Step 3
Temperature, $^\circ\text{C} \pm 2^\circ\text{C}$ ($^\circ\text{F} \pm 5^\circ\text{F}$)	220 (430)	316 (600)	Cool to 93°C (200°F), then remove bonding pressure
Time ± 2 min	60	60	
Bonding pressure, MN/m^2 (psi)	1.4 (200)	1.4 (200)	

The cured panels were given the following post-cure in a dry nitrogen atmosphere:

120 ± 2 min at $343 \pm 2^\circ\text{C}$ ($650 \pm 5^\circ\text{F}$)

IV. Test Specimen Preparation—PQ Adhesive

A. Specimen Description

The polyquinoxaline (PQ) resin was purchased as a solution in m-cresol (15 to 16% solids). This resin, therefore, required further processing in order to prepare it as a fiberglass-supported adhesive. This processing consisted of the following steps:

- (1) A resin mixture of the following composition was prepared:

PQ resin	100 g
Aluminum powder (J. T. Baker Co. No. 0446)	7.5 g

- (2) A section [20.32×25.4 cm (8×10 in.)] of glass fabric (112-A 1100) was dried to constant weight in an air-circulating oven at approximately 121°C (250°F).
- (3) The dried fabric was clamped to a 20.32×25.4 -cm (8×10 -in.) aluminum frame.
- (4) One coat of the resin mixture was applied to both surfaces of the glass fabric.
- (5) The coated fabric was allowed to air-dry at room temperature for 3 days.
- (6) The coated fabric was then dried in an air-circulating oven at $60\text{--}63^\circ\text{C}$ ($140\text{--}145^\circ\text{F}$) for approximately 7 h.
- (7) The process of resin coating and drying was continued until the coated fabric obtained a specific weight of approximately 0.04 g/cm^2 (0.01 oz/in.^2).
- (8) The volatile content of the coated fabric was then determined as follows:

A small section of the coated fabric was heated under nitrogen at $400 \pm 5^\circ\text{C}$ ($750 \pm 10^\circ\text{F}$) for 30 ± 2 min. The weight loss thus obtained established the volatile content of the coated fabric (film adhesive). A volatile content of 20–40% was obtained with the preceding coating technique.

B. Bonding of Lap Shear Panels

Bonded test panels were prepared according to the ASTM D1002 test method. The bonding operation was as follows:

- (1) Prepared 1.3-mm (0.050-in.) titanium panels were primed with a 0.03-mm (1-mil) coat of the aluminum/PQ resin mixture (previously described). The primed panels were allowed to air-dry at room temperature for approximately 16 h. The panels were then air-dried at $60 \pm 2^\circ\text{C}$ ($150 \pm 15^\circ\text{F}$) in an air-circulating oven for approximately 1 h.
- (2) The primed panels and the prepared PQ film adhesive were then assembled into a standard panel layup, as specified in ASTM D1002.
- (3) The panel layup was wrapped in an aluminum foil envelope which was fitted with a dry nitrogen purge. The complete assembly was then placed in a heated platen hydraulic press.
- (4) A 1.4-MN/m^2 (200-psi) bonding pressure was applied to the bonding surfaces of the lap shear panels.
- (5) The panel assembly was then heated under a 1.4-MN/m^2 (200-psi) pressure to $343 \pm 2^\circ\text{C}$ ($650 \pm 5^\circ\text{F}$) (warm-up time approximately 30 min). A nitrogen purge of approximately 0.1 SCMH^4 (3.5 SCFH^5) was continuously maintained.

⁴Standard cubic meters per hour.

⁵Standard cubic feet per hour.

- (6) After 1 h at 343°C (650°F), the temperature of the panel assembly was increased to $399 \pm 2^\circ\text{C}$ ($750 \pm 5^\circ\text{F}$). The nitrogen purge and bonding pressure of 1.4 MN/m^2 (200 psi) were continued. The panels were then cured under these conditions for $3\text{ h} \pm 5\text{ min}$.
- (7) After the curing process, the panel assembly was allowed to cool slowly to room temperature. The panel bonding pressure and the nitrogen purge were maintained.
- (8) After cooling, the panels were machined into standard lap shear test specimens according to the ASTM D1002 test method.
- (9) The cured panels were given the following post-cure in a dry nitrogen atmosphere:

$120 \pm 2\text{ min}$ at $343 \pm 2^\circ\text{C}$ ($650 \pm 5^\circ\text{F}$)

V. Test Specimen Preparation—Epon 913 Adhesive

The EA913 adhesive was a paste-type adhesive. Lap shear specimens were prepared from this adhesive using 1.6-mm (0.062-in.) aluminum (6061-T6) panels. The panels were prepared as outlined in *Section I* of this appendix.

The EA913 adhesive was prepared according to the manufacturer's recommended procedure. The lap shear panels were bonded using a vacuum bagging technique which maintained the bonding pressure. The panels were given the following cure:

$180 \pm 2\text{ min}$ at $82 \pm 2^\circ\text{C}$ ($180 \pm 5^\circ\text{F}$)

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